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**EUROPEAN PATENT APPLICATION**

21 Application number: 85870066.9

51 Int. Cl.<sup>4</sup>: **B 01 J 21/18, C 07 C 85/20,**  
**C 07 F 9/38**

22 Date of filing: 10.05.85

30 Priority: 10.05.84 US 608831  
28.02.85 US 705391

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43 Date of publication of application: 21.11.85  
Bulletin 85/47

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64 Designated Contracting States: **AT BE CH DE FR GB IT**  
**LI LU NL SE**

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54 Improved oxidation catalyst.

57 An improved process is provided for the selective production of secondary amines and primary amines by bringing together under reaction conditions a tertiary amine or a secondary amine with oxygen or an oxygen-containing gas in the presence of an activated carbon catalyst, the improvement which comprises using an activated carbon catalyst wherein oxides have been removed from the surface of the carbon.

**EP 0 162 035 A2**

IMPROVED OXIDATION CATALYSTBackground of the Invention

5 The present invention relates to an improved oxidation catalyst and, more particularly, to a method for enhancing the catalytic activity of activated carbon for use in oxidation reactions.

10 U.S. Patent 4,264,776 discloses and claims a process for preparing secondary amines by catalytic oxidation of tertiary amines with oxygen over carbon catalyst. The catalyst is an activated carbon of the type well known in the art and characterized by high absorptive capacity for gases, vapors, and colloidal solids and relatively high specific surface areas. Activation of commercially available carbon catalysts  
15 is usually achieved by heating the carbon to high temperatures (800°C to 900°C) with steam or with carbon dioxide which brings about a porous particulate structure and increased specific surface area.

20 U.S. Patent 4,072,706 discloses a process for oxidative removal of phosphonomethyl groups from tertiary amines in which a molecular oxygen-containing gas is employed along with an activated carbon catalyst. It is noted that any source or form of carbon can be used as a catalyst or substrate in the process of the disclosed invention.  
25

U.S. Patent 3,969,398 teaches the use of activated carbon in the catalytic oxidation of N-(phosphonomethylimino)diacetic acid. It is stated that the carbon catalysts useful in the claimed  
30 process are available under a large number of trade names.

U.S. Patent 3,497,564 discloses the use of amorphous or graphitic carbon as a catalyst in the oxidative dehydrogenation of alkylbenzenes. It is taught that activated carbon of whatever origin is operable in the process.

Japanese Patent Application 56-17634 discloses an activation method for  $\text{SO}_3/\text{SO}_2$  conversion carbon materials which are useful as reduction catalysts to convert selectively  $\text{SO}_3$  in various gases, such as air and exhaust, to  $\text{SO}_2$ . Carbon materials, such as cylindrical activated carbon, are treated with an oxidizing acid, e.g., nitric acid, followed by heat treatment at  $300^\circ\text{C}$  to  $700^\circ\text{C}$  under an inert gas.

U.S. Patent 4,158,643 teaches a method for oxidative modification of an activated carbon support in which oxygen is added to the surface of the activated carbon, and then the carbon support is impregnated with an inert hydrophobic compound. The carbon support, which may be any commercially available activated carbon for vapor phase activation use, is useful in oxidizing carbon monoxide in the presence of sulfur dioxide for an extended period of time.

U.S. Patent 3,243,383 teaches a method for regenerating spent catalysts which have been used for polymerizing olefins to liquid products. According to the disclosure, spent cobalt oxide on carbon catalyst is heated in an inert atmosphere, cooled, and then treated with nitric acid, nitric oxide, or nitrogen dioxide.

None of the foregoing references suggests that the surface of a carbon catalyst, particularly where acidic and basic surface oxides can be present, can play an important role in amine oxidation rates.

Summary of the Present Invention

The present invention provides a method for preparing activated carbon for catalytically oxidizing tertiary amines or secondary amines in the presence of oxygen or an oxygen-containing gas to selectively produce secondary or primary amines which comprises the step of treating the carbon catalyst to remove oxides from the surface thereof. To accomplish the removal of surface oxides, a treatment sequence is followed which comprises subjecting the carbon material to an oxidizing agent, such as nitric acid,  $\text{CrO}_3$ ,  $\text{H}_2\text{O}_2$ , hypochlorite and the like, or an oxidant gas, such as  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{O}/\text{NH}_3$ ,  $\text{CO}_2$ ,  $\text{NO}_x$ , air, etc. and then pyrolyzing it in an oxygen-free atmosphere at a temperature in the range of about  $500^\circ\text{C}$  to  $1500^\circ\text{C}$ .

However, the treatment can also be accomplished by simultaneously pyrolyzing the carbon material in the presence of  $\text{NH}_3$  and an oxygen-containing gas that will react with the oxides on the surface of the carbon at pyrolyzing temperatures. Suitable oxygen-containing gases include steam,  $\text{NO}_x$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{SO}_2$  and mixtures of such gases.

Thus, it can be seen that in another embodiment of this invention there is provided an improved process for the selective production of secondary amines and primary amines by bringing together under reaction conditions a tertiary amine or a secondary amine with oxygen or an oxygen-containing gas in the presence of an activated carbon catalyst, the improvement which comprises using an activated carbon catalyst wherein oxides have been removed from the surface thereof.

As used herein the term "oxides" is intended to mean carbon functional groups which contain oxygen as well as hetero atom functional groups which contain

oxygen. Other hetero atom functional groups which do not contain oxygen may also be removed from the surface of the carbon material during treatment.

Activated carbons prepared according to the process of this invention demonstrate unexpectedly improved activity, i.e., reaction rates, in the catalytic oxidation of tertiary amines to selectively produce secondary amines. Moreover, the oxidative removal of carboxymethyl and phosphonomethyl groups from tertiary amines and secondary amines and the catalytic oxidation of N-(phosphonomethylimino)-diacetic acid can be significantly enhanced using a carbon catalyst treated according to this invention, without regard to the kind of carbon material employed.

Detailed Description of the Invention

According to the present invention, the activity of carbon as a catalyst in the oxidation of tertiary amines to secondary amines and in the oxidation of secondary amines to primary amines can be greatly enhanced if the carbon material is first subjected to a treatment process to remove surface oxides. In carbon catalyzed oxidation reactions, an analysis of the catalysis mechanism tends to suggest a possible correlation between catalyst activity and surface area and/or pore size distribution. It has now been discovered that the presence of basic and acidic oxides on the surface of the carbon material can play a significant role in the oxidation process. Although applicant does not wish to be bound by any particular theory, it is believed that the catalytic activity of the catalyst can be substantially increased if the acidic oxides are removed from the surface of the carbon.

U.S. Patent 4,264,776, the teachings of which are incorporated herein by reference, describes a wide variety of carbon materials which can be used in practicing this invention. Ordinarily the carbon

catalyst is a commercially available activated carbon with a carbon content ranging from about 10% for bone charcoal to about 98% for some wood chars and nearly 100% for activated carbons derived from organic polymers. The noncarbonaceous matter in commercially available carbon materials will normally vary depending on such factors as precursor origin, processing, and activation method. For example, inorganic "ash" components containing aluminum and silicon can be present in large amounts accompanied by certain alkali metals and alkaline earths. The latter grouping influences the acidity-basicity characteristics of the activated carbon. Among other inorganic elements often found in activated carbons are iron and titanium. Depending on raw material origin and activation procedure, large amounts of oxygen can be present along with lesser amounts of hydrogen, nitrogen, sulfur, and other organic functional groups. Despite the wide variety of elements and impurities which can comprise an individual commercially available carbon material, the process of this invention is applicable to all commercially available activated carbon catalyst materials.

Following is a listing of some of the activated carbons which have demonstrated enhanced activity after treatment according to this invention. The list is presented for illustration and should not be interpreted as limiting the applicability of this invention. Preferably, the carbons are in the form of powders, although granules or any other suitable particulate form or shape can be employed in practicing this invention.

Trade Name  
Darco G-60 Spec

Sold By  
ICI-America  
Wilmington, Delaware

	<u>Trade Name</u>	<u>Sold By</u>
	Darco X	ICI-America Wilmington, Delaware
5	Norit SG Extra	Amer. Norit Co., Inc. Jacksonville, Florida
	Norit EN4	Amer. Norit Co., Inc. Jacksonville, Florida
	Norit EXW	Amer. Norit Co., Inc. Jacksonville, Florida
10	Norit A	Amer. Norit Co., Inc. Jacksonville, Florida
	Norit Ultra-C	Amer. Norit Co., Inc. Jacksonville, Florida
	Norit ACX	Amer. Norit Co., Inc. Jacksonville, Florida
15	XZ	Amer. Norit Co., Inc. Jacksonville, Florida
	NW	Barnebey-Cheney Columbus, Ohio
20	JV	Barnebey-Cheney Columbus, Ohio
	BL Pulv.	Barnebey-Cheney Columbus, Ohio
25	PWA Pulv.	Pittsburgh Activated Carbon Div. of Calgon Corporation Pittsburgh, Pennsylvania
	PCB Fines	Pittsburgh Activated Carbon Div. of Calgon Corporation Pittsburgh, Pennsylvania
30	P-100	Pittsburgh Activated Carbon Div. of Calgon Corporation Pittsburgh, Pennsylvania
	Nuchar CN	No. Amer. Carbon, Inc. Columbus, Ohio
35	Nucher C-1000N	Westvaco Corporation Carbon Department Covington, Virginia
		Westvaco Corporation Carbon Department Covington, Virginia



	<u>Trade Name</u>	<u>Sold By</u>
	Nuchar C-190A	Westvaco Corporation Carbon
	Nuchar C-115A	Department Covington, Virginia
5	Code 1551	Westvaco Corporation Carbon
		Department Covington, Virginia
		Baker and Adamson Division of
		Allied Amer. Norit Co., Inc.
		Jacksonville, Florida
	Norit 4 x 14 mesh	Amer. Norit Co., Inc.
10	G1-9615	Jacksonville, Florida
		Barnebey-Cheney
		Columbus, Ohio
	VG-8408	Barnebey-Cheney
		Columbus, Ohio
15	VG-8590	Barnebey-Cheney
		Columbus, Ohio
	NB-9377	Barnebey-Cheney
		Columbus, Ohio
	Grade 235	Witco Chemical Corp.
20		Activated Carbon Div.
		New York, New York
	Grade 337	Witco Chemical Corp.
		Activated Carbon Div.
		New York, New York
25	Grade 517	Witco Chemical Corp.
		Activated Carbon Div.
		New York, New York
	Grade 256	Witco Chemical Corp. Activated
		Carbon Div. New York, New York
30	Columbia SXAC	Union Carbide New York, New
		York

In practicing this invention, the treatment  
 process can be accomplished by a single or a multi-  
 step scheme which in either case results in an overall  
 35 chemical reduction of oxides on the carbon surface;  
 i.e., a reduction or removal of acidic oxides from the  
 carbon surface.

In a two-step scheme, the carbon material can be first treated with an oxidizing agent such as, for example, liquid nitric acid, nitrogen dioxide,  $\text{CrO}_3$ , air, oxygen,  $\text{H}_2\text{O}_2$ , hypochlorite, or a mixture of gases obtained by vaporizing nitric acid. The treatment can be accomplished using either a gas or a liquid oxidizing agent. Where a liquid is used, concentrated nitric acid containing from about 10 to about 80 gm  $\text{HNO}_3$  per 100 gm of aqueous solution is preferred. Preferred gaseous oxidants include oxygen, nitrogen dioxide, and nitric acid vapors. A particularly effective oxidant is nitric acid in the vapor phase which includes nitric acid carried into the vapor phase by an entraining gas as well as the vapors obtained by distilling liquid nitric acid. With a liquid oxidant, temperatures from about  $60^\circ\text{C}$  to about  $90^\circ\text{C}$  are appropriate, but with gaseous oxidants, it is often advantageous to use temperatures of about  $50^\circ\text{C}$  to about  $500^\circ\text{C}$  or even higher for the treatment step.

The treatment can be achieved by placing carbon from a manufacturer in a round bottom flask which contains a magnetic stirring bar. Liquid nitric acid is selected as the oxidizing agent for illustration. The amount of carbon used is determined by the percent carbon load desired (% carbon load = gm of carbon used per 100 ml of nitric acid solution) and the nitric acid solution volume to be used. Ordinarily, 1 to 200 gm of carbon per 100 ml of nitric acid or other liquid oxidizing agent is satisfactory. Temperature control can be provided by any suitable means. A condenser and scrubber can be connected to the round bottom of the flask as desired. A calculated volume of water, preferably deionized water, is added to the carbon, followed by sufficient 69-71% nitric acid to achieve the desired nitric acid solution. The carbon and

nitric acid solution are then stirred for the desired period at the desired temperature. Experimental results indicate that carbon load, temperature, nitric acid concentration, etc. in the first treatment step  
5 are not particularly critical to achieving the desired oxidation of the carbon material and thus may be governed by convenience over a wide range. The highest possible carbon load is preferred for economic reasons.

After stirring the carbon is filtered, and  
10 the resulting wet cake may or may not be washed and/or dried prior to pyrolysis.

The time during which the carbon is treated with the oxidant can vary widely from about 5 minutes to about 10 hours. Preferably, a reaction time of  
15 about 30 minutes to about 6 hours is satisfactory. When concentrated nitric acid is the oxidant, a contact time of about 30 minutes to about 3 hours is satisfactory.

In a second step, the oxidized carbon  
20 material is pyrolyzed, i.e., heat treated, at a temperature in the range of about 500°C to about 1500°C, preferably from about 800°C to 1200°C. In one embodiment of this invention, the pyrolysis is conducted in an atmosphere such as nitrogen  
25 containing small amounts of steam or carbon dioxide, which is believed to aid in the pyrolysis. As will occur to those skilled in the art in view of this disclosure, the oxides will be removed from the surface of the carbon at pyrolysis temperatures, but  
30 the presence of oxygen-containing gases such as steam or carbon dioxide should be avoided as the carbon cools below pyrolysis temperatures to avoid the re-formation of surface oxides. Accordingly, it is preferred to conduct the pyrolysis in an inert gas  
35 atmosphere, such as nitrogen, argon or helium.

Wet cake or dry carbon is placed in a ceramic pyrolysis dish which together are placed in a quartz tube. In one embodiment of this invention, nitrogen gas is passed through water at about 70°C, then through the quartz tube during pyrolysis. In an alternate embodiment, a dry, static nitrogen atmosphere is maintained after flushing the quartz tube with several tube volumes of dry nitrogen prior to pyrolysis. The quartz tube containing the pyrolysis dish is placed in a suitable pyrolyzer apparatus at about 930°C for the desired period, followed by cooling while maintaining the nitrogen atmosphere.

Pyrolysis can last anywhere from about 5 minutes to 60 hours, although 10 minutes to 6 hours is normally satisfactory. The shorter times are preferred for economic reasons because, as might be expected, continued exposure of the carbon to elevated temperatures for prolonged periods can result in a poor carbon catalyst for the oxidation. In addition, although applicant does wish to be bound by any particular theory, it is believed that prolonged heating at pyrolysis temperatures favors the formation of graphite, and it is believed that graphite is not as satisfactory as activated carbon for the oxidative conversion of tertiary and secondary amines to secondary and primary amines. It is preferred that the pyrolysis occurs in a slightly moist atmosphere or an atmosphere which contains  $\text{NH}_3$  as this appears to produce a more active catalyst in a shorter time.

In a preferred embodiment of this invention, the treatment is accomplished in a single step by pyrolyzing the carbon material as described above while simultaneously passing a gas stream comprised of  $\text{NH}_3$  and an oxygen-containing gas e.g.,  $\text{H}_2\text{O}/\text{NH}_3$ , through the carbon. Although it is not a

critical feature of this invention, the flow rate of the gas stream should be fast enough to achieve adequate contact between fresh gas reactants and the carbon surface, yet slow enough to prevent excess carbon weight loss and material waste. Many  $\text{NH}_3$ /oxygen-containing gas mixtures can be used such as, for example,  $\text{NH}_3/\text{CO}_2$ ,  $\text{NH}_3/\text{O}_2$ ,  $\text{NH}_3/\text{H}_2\text{O}$  and  $\text{NH}_3/\text{NO}_x$ , provided the gas mixture achieves the desired result. Ordinarily, the oxygen-containing gas/ $\text{NH}_3$  ratio can range from 0:100 to 90:10. Furthermore, nitrogen can be used as a diluent to prevent severe weight loss of the carbon in high oxygen-containing gas concentrations. Ammonia is a basic gas, and, as such, is believed to assist the decomposition of the various oxide groups on the surface of the carbon material. Any other chemical entity which will generate  $\text{NH}_3$  during pyrolysis should also prove satisfactory as an  $\text{NH}_3$  source. For economic reasons an  $\text{NH}_3/\text{H}_2\text{O}$  gas stream is most preferred in practicing the process of this invention.

The carbon materials treated according to the process of this invention, when used in the catalytic oxidation of tertiary amines and secondary amines, demonstrate substantially increased activity, i.e., faster reaction rates, than commercially available activated carbons. Reaction rates, for example, can be increased up to 30 times and higher the rate obtainable with otherwise untreated commercial activated carbon catalysts, all other oxidation reaction conditions remaining unchanged. Surprisingly, even carbons which are initially inactive, such as carbon black and sugar charcoal, for example, can be activated according to the process of this invention. In addition to the catalytic oxidation of tertiary and secondary amines, carbon catalysts prepared according to this invention improve the oxidative removal of carboxymethyl groups and phosphonomethyl groups from tertiary amines as well as the catalytic oxidation of N-(phosphonomethyl-imino)diacetic acid.

The present invention can be more clearly illustrated by the following examples.

Example 1

5 This example illustrates the improved results that are obtained by the catalysts of this invention when used to convert a tertiary amine to a secondary amine.

10 Twenty-two powdered activated carbon samples were obtained from commercial sources, and a portion of each was subjected to the two-step treatment process described above. Approximately 12 grams of the carbon were placed in a 250 milliliter round-bottomed flask equipped with a magnetic stirrer. Then, 100 milliliters of 18.1 percent nitric acid was  
15 added to the flask, and the contents were heated to about 85°C to about 100°C for six hours. The flask was allowed to cool to room temperature and the carbon was separated from the acid solution by filtration on a porous frit. The carbon was dried overnight in an  
20 oven at 85°C, then placed in a ceramic pyrolysis dish. The dish and the carbon were placed in a quartz tube. Dry nitrogen was passed through the tube while heating the tube and contents to approximately 930°C. Heating was continued for one hour. The heating was discon-  
25 tinued and the tube and contents were allowed to cool to room temperature while maintaining the flow of nitrogen over the carbon during cooling.

A portion of the treated and untreated carbon from each sample was then used as a catalyst in the  
30 oxidation of 7.3 gm N-(phosphonomethylimino)diacetic acid in 92 ml of water to produce N-phosphonomethylglycine. The catalyst charge was 1.2 gm for each run. Data obtained from observing each reaction are shown below in Table I. The amine oxidation was performed  
35 in an autoclave made by Autoclave Engineers at 85°C and 50-55 psig oxygen pressure using an oxygen flow rate through the autoclave of 200 ml/min.

TABLE I

		<u>Amine Oxidation Time (Minutes)</u>	
		<u>Treated</u>	<u>Untreated</u>
	<u>Carbon Type</u>	<u>Catalyst</u>	<u>Catalyst</u>
5	Calgon C	20	40
	Calgon BL	17	38
	Calgon RC	11	50
	Darco GFP	15	36
	Darco FM-1	10	66
10	Darco TRS	13	58
	Darco S51	18	80
	Darco S-51FF	10	55
	Darco S-51K	13	113
	Darco BG	13	40
15	Darco KB	14	136
	Darco FM-1	11	66
	Norit W20	16	69
	Norit F	15	61
	Norit FQA	23	>100
20	Norit SA4	11	39
	Norit PN3	11	36
	Norit A	8	46
	Nuchar		
	Aqua Pac	18	75
25	Nuchar		
	Aqua S	10	57
	Nuchar		
	Experimental "A"	12	29
	Nuchar		
30	Experimental "B"	10	85

Example 2

Six portions of Norit W20 carbon were subjected to the two-step treatment of example 1 except that the pyrolysis time was varied from one to six hours. Results are shown in Table 2.

TABLE 2

<u>Pyrolysis</u> <u>time (hours)</u>		<u>Amine Oxidation Time (Minutes)</u>	
		<u>Treated</u> <u>Catalyst</u>	<u>Untreated</u> <u>Catalyst</u>
10	1	16	69
	2	11	-
	3	11	-
	4	11	-
	5	6	-
15	6	10	-



Example 3

In a 1.9 cm I.D. x 40.6 cm length quartz tube is placed 2.5 gm of Calgon C 450 activated carbon. The tube is connected to a gas stream resulting from sparging a 70 to 100 ml/min. N<sub>2</sub> stream through a 70°C, 10% NH<sub>4</sub>OH aqueous solution. The quartz tube is then placed in a preheated 30.5 cm tubular furnace and pyrolyzed at 930°C for 60 min. and cooled to room temperature under a dry N<sub>2</sub> atmosphere without contacting any air.

The above carbon is used to oxidize various tertiary amines to secondary amines in a 300 ml autoclave made by "Autoclave Engineering" at 85°C,  $3.44 \times 10^5$  N/m<sup>2</sup> pressure and 200 ml/min. O<sub>2</sub> flow rate. The samples are analyzed by HPLC. The concentration of the reactant, catalyst load, and reaction times of treated catalyst vs. untreated catalyst of various tertiary amines are listed in Table 3 along with the reaction end point which can be determined by any one of several convenient methods known to those skilled in the art.

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TABLE 3

Amine Oxidation Time (Minutes)

	<u>Reactant</u>	<u>Reactor-Load</u>	<u>Amine Oxidation Time (Minutes)</u>		
			<u>Untreated Catalyst</u>	<u>Treated Catalyst</u>	<u>Desired Product</u>
5	Nitrilotriacetic acid	4 gm Reactant	>100	19.5	Iminodiacetic acid
		96 ml H <sub>2</sub> O			
		0.2 gm Catalyst			
		2.0 gm Reactant			
		98 ml H <sub>2</sub> O			
10	N-phosphonomethyl-N-(n-propyl)glycine	0.1 gm Catalyst	>60	10	N-n-propyl-aminomethyl-phosphonic acid
		7.5 gm Reactant			
		92 ml H <sub>2</sub> O			
		0.2 gm Catalyst			
		5 gm Reactant			
15	N-phosphonomethylimino-diacetic acid	95 ml H <sub>2</sub> O	>400	33	N-phosphono-methylglycine
		0.2 gm Catalyst			
		5 gm Reactant			
		95 ml H <sub>2</sub> O			
		0.2 gm Catalyst			
15	Trisphosphonomethylamine N(CH <sub>2</sub> PO <sub>3</sub> H <sub>2</sub> ) <sub>3</sub>	5 gm Reactant	>100	61.5	Bisphosphono-methylamine
		95 ml H <sub>2</sub> O			
		0.2 gm Catalyst			

Example 4

In a 1.9 cm I.D. x 35.6 cm long quartz tube was placed 3.55 gm of Norit W-20 activated carbon. The tube was connected to streams of 50 ml/min. of  $\text{NH}_3$  gas and 89 ml/min. of steam and then placed in a preheated 30.5 cm tubular furnace and pyrolyzed at  $930^\circ\text{C}$  for 30 minutes. The tube was then cooled to room temperature under a dry  $\text{N}_2$  atmosphere without any contact with air. The resulting carbon gave 54% weight loss.

Then, 7.3 gm of N-(phosphonomethylimino)diacetic acid, 1.2 gm of the above catalyst and 92 ml of  $\text{H}_2\text{O}$  were mixed in a 300 ml autoclave made by "Autoclave Engineers" and oxidized at  $70^\circ\text{C}$ ,  $3.44 \times 10^5 \text{ N/m}^2$   $\text{O}_2$  pressure and 200 ml/min.  $\text{O}_2$  flow rate. The reaction finished at 9.7 min. The rate of reaction using the treated catalyst was 11.4 times faster than the reaction using the untreated catalyst.

CLAIMS

1. A process for the selective production of secondary amines and primary amines by bringing together under reaction conditions a tertiary amine or a secondary amine with oxygen or an oxygen-containing gas in the presence of an activated carbon catalyst, characterised in that the activated carbon catalyst is an activated carbon catalyst wherein oxides have been removed from the surface thereof.
2. A process of Claim 1 wherein a secondary amine is produced from a tertiary amine.
3. A process of Claim 2 wherein the tertiary amine is an N-phosphonomethyl tertiary amine.
4. A process of Claim 3 wherein the tertiary amine is N-(phosphonomethylimino)diacetic acid.
5. A process of Claim 4 wherein N-phosphonomethylglycine is produced.
6. An activated carbon catalyst for catalytically oxidizing tertiary amines and secondary amines in the presence of oxygen or an oxygen containing gas to selectively produce secondary amines and primary amines wherein the carbon catalyst has been treated to remove oxides from the surface thereof.
7. The activated carbon catalyst of Claim 6 wherein the treatment comprises the steps of subjecting the carbon to an oxidizing agent and then pyrolyzing the carbon in an oxygen-free atmosphere at a temperature in the range of about 800°C to 1200°C.
8. The activated carbon catalyst of Claim 6 wherein the treatment comprises pyrolyzing the carbon at a temperature in the range of about 800°C to 1200°C while simultaneously passing a gas stream comprising  $\text{NH}_3$  and an oxygen-containing gas over the carbon.

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9. The activated carbon catalyst of Claim 8 wherein the oxygen-containing gas is selected from  $H_2O$ ,  $NO_x$ ,  $O_2$ ,  $CO_2$ ,  $SO_2$  and mixtures thereof.

10. The activated carbon catalyst of Claim 9 wherein said gas stream is  $NH_3/H_2O$ .